Simple laboratory-made system for the determination of C_2–C_7 hydrocarbons relevant to photochemical smog pollution

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Abstract

A simple gas chromatographic system suitable for determining volatile organic compounds from C_2 to C_7 in air is described. It consists of a capillary cold trap filled with graphitic carbon, a thermodesorbing device, a capillary gas chromatograph equipped with an alumina column and a flame ionization detector. Dry, as well as humid, air samples can be analysed with our system. Up to 2-l samples of air can be enriched on our trapping device by using Nafion membranes for removing water. Direct analysis of air samples is possible by enriching 250 ml on the carbon trap. The recovery, sensitivity and linearity of our system have been checked with standard mixtures and real samples. The performances have been compared with those afforded by a commercially available instrument exploiting a different enrichment procedure. The results obtained show that our analyser can be successfully applied to determinations of C_2 to C_7 hydrocarbons present in air samples at levels of 0.01 ppb (v/v). © 1997 Elsevier Science B.V.

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1. Introduction

Volatile organic compounds (VOCs) play a relevant role in atmospheric chemistry because some of them act as precursors of photochemical smog formation (VOC-OX), while others (VOC-TOX) can be directly toxic to humans [1,2]. Specific components (like chlorofluorocarbons) also contribute to stratospheric ozone depletion (VOC-STRAT) and greenhouse warming (VOC-CLIM) [1,3]. The different spatial domains (local, synoptic and global), in which the adverse effects produced by the various classes of VOC can be detected, require that dedi-

cated approaches are used for their monitoring in air [2].

To assess the role played by VOC-OX in determining the levels of ozone and photooxidants that can be reached in urban and suburban airsheds and to design strategies aimed at reducing photochemical smog pollution at a local and synoptic level, quantitative determinations of hydrocarbons, characterised by a high photochemical ozone-creating potential [4], are required [5]. Lists of VOC-OX to be determined with high priority have been proposed in the USA [5] and Europe [6]. Although some differences exist between these two lists, core compounds to be detected are alkanes, alkenes, alkynes and arenes from C_2 to C_7.

Several gas chromatography–flame ionization de-

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tection (GC–FID) methods based on the use of capillary columns capable of separating all compounds of interest have been developed and used for identifying and quantifying VOCs present in air samples. Either capillary columns coated with Al_2O_3 and inorganic salts (KCl or Na_2SO_4) [7–9] or silicone fluids [5,10,11] have been used for separating these core compounds. The sequential use of both columns [12] has also been proposed, to extend the range of carbon numbers to be determined to above C_8. To collect a sufficient amount of mass for quantitative analysis, VOC-OX are adsorbed on traps filled with solid sorbents or glass beads maintained at low temperatures (usually liquid argon or nitrogen). Various devices are used to remove water from the air stream in order to avoid plugging of the capillary column during the desorption step. Either cold traps [5,7,11], drying salts [13] or ion-exchange membranes are used [12,14] for this purpose. In some instances, cryofocusing systems are inserted at the column inlet to prevent band spreading of the GC peaks [7,11,13]. Automated instruments exploiting cryogenic trapping of VOC-OX and their GC–FID determination by thermal desorption are now commercially available and commonly used in monitoring stations [15]. Their adoption does not necessarily imply, however, that the determination of VOC-OX is easy and free from practical problems and analytical artefacts. The adoption of ion-exchange membranes for removing water from the air stream has not definitely been proven to be free from memory effects caused by adsorption and/or partition of hydrocarbons on the membrane walls. Quantitative collection of very volatile compounds (such as ethane and ethylene) is still uncertain and losses can take place, especially when cryofocusing steps are introduced in the analytical sequence. In addition to technical problems, some automated instruments are quite expensive to run because the consumption of liquid nitrogen is high (500 to 1000 l/week) and the presence of skilled personnel cannot be avoided. Because of these difficulties, the development of manually operated systems capable of ensuring good collection and recovery of VOC-OX is still pursued by laboratories involved in monitoring the atmosphere. Sensitive, precise and accurate VOC analysers are particularly needed in background stations where concentrations to be detected are so low that even

small sampling or analytical artefacts can introduce large errors in the analysis.

In this paper, a method suitable for the determination of C_2 to C_7 hydrocarbons in air is presented. The quantitative collection of very volatile compounds and their complete desorption is achieved by using a micro-trap filled with a graphitic adsorbent kept at $-150°C$. Due to the small internal volume of the system, no cryofocusing steps are needed for injecting the sample. The use of ion-exchange membranes for water removal can be avoided if volumes smaller than 250 ml are enriched.

2. Experimental

A schematic diagram of the apparatus used for the analysis of C_2–C_7 hydrocarbons is reported in Fig. 1. The instrument comprises a micro-trap connected to a pneumatically operated eight-port valve (Model Bimatic, Fisons, Milan, Italy), allowing the transfer of the sample from the trap to the gas chromatograph by thermal desorption. The enriching device is made
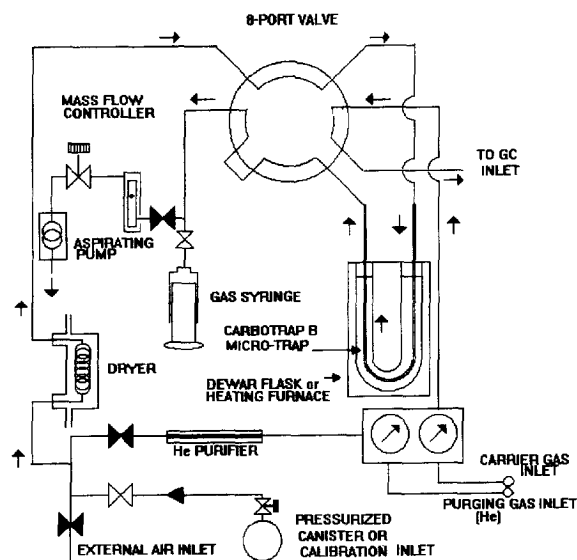

Fig. 1. Schematic diagram of the laboratory-made VOC-OX analyser: The scheme refers to the sampling step from passivated canisters. By closing the open valves (empty symbols), the collection of external air can be performed. Desorption of the enriched sample is achieved by switching the eight-port valve and by replacing the cryogenic vessel with the heating furnace.

of glass and is a U-shaped tube with an external diameter of 6 mm. The trap is 25 cm long. The inlet of the trap (10 cm) has an internal diameter of 1 mm, whereas the remaining portion is smaller (0.5 mm), to reduce the dead volume at the column inlet. The last 5 cm of the inlet tube are filled with small quantities (0.005 g) of Carbopack B (Supelco, Bellefonte, PA, USA) particles with mean diameters ranging from 100 to 350 μm. The carbon adsorbent is kept in place by quartz wool. Stainless-steel tubes (0.5 mm I.D.×1.5 mm O.D.) are used for connecting the trap outlet to the GC column. Larger tubes (1 mm I.D.×2 mm O.D.) are used for all other connections. A 1.5-m long Nafion tube (Perma Pure Products, Oceanport, NJ, USA) can be inserted in the sampling lines for evaluating the performance of the system with and without water. Ultrapure helium (provided by Air Liquide, Milan, Italy), filtered using Carbosieve G (Supelco) traps, is used as the carrier gas and for the transfer of the sample from the trap to the GC column.

The system is designed in order to make possible both on-line and off-line sampling of VOC-OX. In the former case, an aspirating pump and a flowmeter are connected to the sampling trap. In the latter case, the sample, collected in passivated canisters (Sierra Andersen, Atlanta, GA, USA), is transferred into the micro-trap and the enriched volume is measured using a 250-ml glass syringe. In both cases, a flow-rate of 50 ml/min is maintained through the micro-trap.

The micro-trap is cooled using a Dewar flask (1 l volume) filled with liquid nitrogen. A temperature of −150°C is obtained by separating the glass tube from the liquid nitrogen with a metal chamber. The desired temperature is reached 15 min after the micro-trap is immersed in the Dewar flask. A space of 0.5 cm is maintained between the internal walls of the chamber and the collecting trap.

A constant flow (15 ml/min) of helium is passed through the micro-trap during the desorption and pre-cleaning steps. Thermal desorption of the adsorbed compounds and their transfer to the GC column is achieved by rapidly removing the micro-trap from the Dewar flask and by immersing it in a furnace that is constantly maintained at 300°C. Although it takes the sample 3 min to reach the temperature of the furnace, complete desorption of

the sample is achieved after 40 s when a temperature of 150°C is reached in the micro-trap. The same furnace is used for cleaning the adsorbent before the sampling step.

The sampling–desorption unit is connected to a Carlo Erba (Milan, Italy) capillary gas chromatograph (Fractovap series 4160) through a 15-cm stainless steel capillary tube (0.50 mm I.D.). A 50-m capillary column, internally coated with Al_2O_3 and Na_2SO_4, is used for the separation of C_2–C_7 hydrocarbons. The internal diameter of the column is 0.53 mm. The column was supplied by Chrompack (Middelburg, Netherlands). The flow-rate of the carrier gas is 2.5 ml/min. After sample desorption, the column is maintained at 60°C for 3 min. The column temperature is then raised to 200°C at a rate of 3°C/min and is kept at isothermal temperature for 30 min. Although this program limits the analysis of VOC-OX to toluene, it allows a good separation of eluted compounds and a more accurate evaluation of the peak area. A faster program allows the determination of C_8 aromatic hydrocarbons. Detection of VOC-OX is performed by FID using a Model 25 sensor supplied by Carlo Erba. A Chromatopac C-R3A (Shimadzu, Kyoto, Japan) is used for peak integration. An oil-free pump is used for pressuring the passivated canisters. It was kindly provided by the Norsk Instituut for Luftforskining (Kjeller, Norway). Before and after collection, the passivated canisters are evacuated for 30 min at a temperature of 60°C. The sampling procedure and frequency used for VOC-OX collection in air are those prescribed by the EMEP [16].

Standard mixtures of VOC-OX for calibrating the instrument were supplied by SIAD (Bergamo, Italy) in 20-l bottles that were pressurised at 150 bar with dry nitrogen. They contained nineteen different compounds, from methane to toluene, at 50.1 ppb (v/v) (ppbv) each. The constancy of the standard mixture was checked weekly by using a commercially available analyser (Chrompack VOC-Air analyser). Bottles were found to be stable for twelve months. They were diluted with helium to calibrate the laboratory-made instrument at the concentrations existing in air (2–5 ppbv). The performances of the instrument were also checked with unknown mixtures provided by the Air Pollution Laboratory of the Institute of Applied Environmental Research (APL)

of the Stockholm University, Sweden. Gas mixtures were distributed as part of an Intercomparison Exercise within the laboratories participating in the EMEP Program [16]. On-line and off-line air samples were collected in the suburban station of Montelibretti, located 30 km away from the centre of Rome.

3. Results and discussion

The first approach was aimed at verifying the performances of the sampling and preconcentration unit. Specific attention was focused on very volatile components, as the ability of Carbotrap B to retain volatile components with a carbon number higher than five (at ambient temperature) was clearly demonstrated in previous studies [17]. This adsorbent was also found to be suitable for our purposes because the non-specific nature of the active sites, the low specific surface area (80 m^2 g^{-1}) and the

lack of pores allowed complete desorption of hydrocarbons with a carbon number higher than ten, at temperature lower than 250°C, and thermal decomposition of enriched compounds was largely prevented. Although the use of non-graphitic and porous carbons (like activated charcoals with specific surface areas >1000 m^2 g^{-1}) allows one to retain very volatile components at ambient temperature, the desorption of compounds with a carbon number larger than ca. five is difficult at temperatures lower than 350–400°C. Under these conditions, possible decomposition of heavy components can take place on active surfaces by simulating the presence of very volatile components (ethene and ethane) in the chromatogram.

To be sure that ethane, ethylene, acetylene, propane and propylene were completely retained on Carbopack B, the temperature of the micro-trap was lowered until partial retention of methane was achieved. At −150°C, it was found that detectable fractions (10–17%) of methane were collected by the adsorbent. The presence of the methane peak in the chromatogram was useful for verifying the correctness of the procedures used for the collection and desorption of VOC-OX. The lack of methane was suggestive of possible losses of very volatile components during sampling, whereas the splitting of methane into well-separated peaks was indicative of bad transfer from the trap to the column.
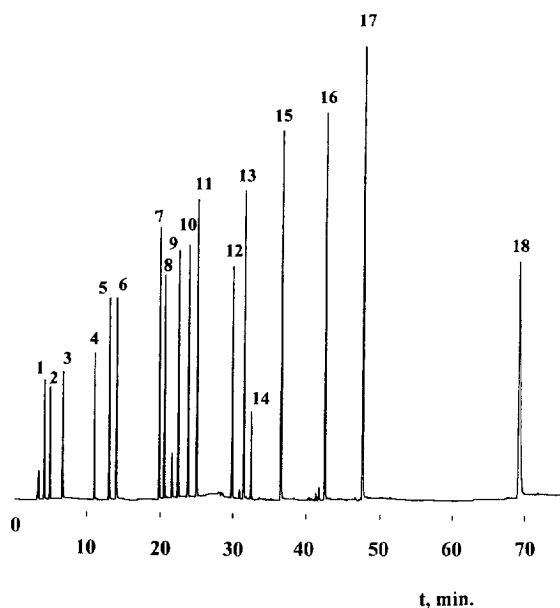
The recovery of eighteen hydrocarbons, ranging

Fig. 2. Gas chromatogram of a standard mixture of eighteen VOC-OX, ranging from ethane to toluene. Peak identification: (1) ethane; (2) ethene; (3) propane; (4) propene; (5) isobutane; (6) n-butane; (7) trans-2-butene; (8) 1-butene; (9) cis-2-butene; (10) 2-methylbutane; (11) n-pentane; (12) trans-2-pentene; (13) 1-pentene; (14) cis-2-pentene; (15) n-hexane; (16) 1-hexene; (17) n-heptane and (18) toluene.

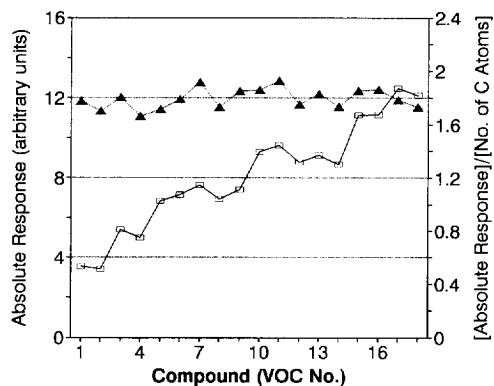Fig. 3. VOC-OX responses of C_2–C_7 hydrocarbons as measured in our analyzer. Squares are used for the absolute FID response, whereas triangles refer to the normalized response. The number of compounds is the same as that reported in Fig. 2.

from C_2 to C_7, was verified by passing 250 ml of a standard solution containing 5 ppbv of each component into the collection trap. The chromatographic profile obtained from the analysis of the standard

mixture is shown in Fig. 2. To find out whether losses of very volatile components occurred, both the absolute (i.e. peak area divided by the concentration of the compound) and the normalized response (i.e. the absolute response divided by the number of carbon atoms present in the molecule) were reported in the figure. Since the absolute FID response of alkanes, alkenes and alkynes linearly increases with the number of carbon atoms in a molecule, lower normalized responses should have been recorded for compounds that were lost during the enriching step. The data reported in Fig. 3 show that, within the experimental errors, both quantitative collection and complete desorption of all components were obtained with the carbon micro-trap. It was found also that alkene and aromatic compounds provided a FID response that was ca. 8% lower than that of the corresponding alkanes.

The ability to provide accurate results in the analysis of diluted atmospheric samples was first tested through a Laboratory Intercomparison Exercise, organised among the various laboratories involved in VOC-OX monitoring in the EMEP network [16]. The results obtained in the analysis of light hydrocarbons (see Fig. 4) showed that small deviations from the median were obtained with our system. Only propene showed a deviation that was larger than 10%.

To confirm these results and also to evaluate the performances of our system in the collection and desorption of high molecular mass compounds, further tests were made. The response given by our
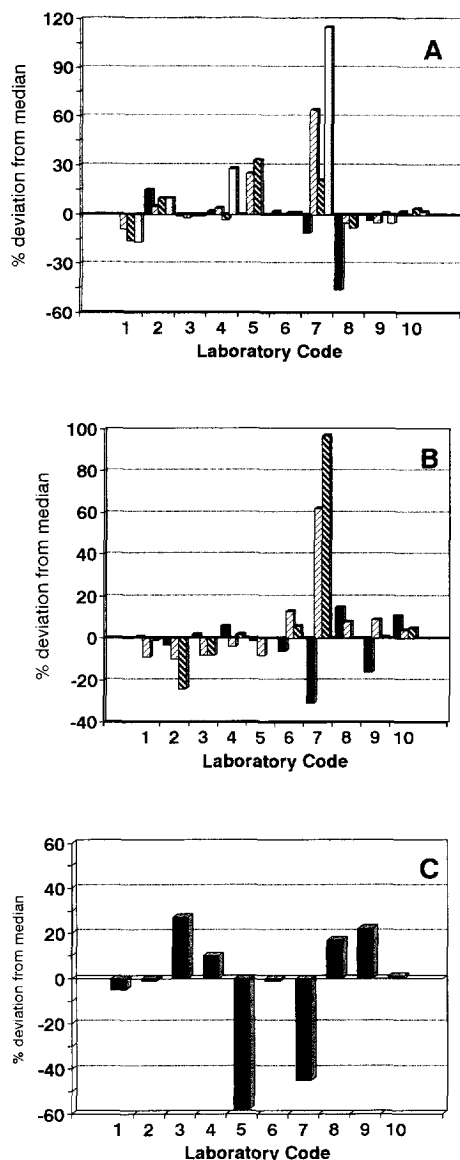
Fig. 4. Results of an EMEP VOC Intercomparison Exercise. The participating laboratories are identified by different code numbers. Number 6 refers to the results obtained by our laboratory. Bars are used to show the percentage deviation of each laboratory from the average value. (A) C_2–C_5 n-alkanes; (■) ethane, (◆) propane, (◈) n-butane and (□) n-pentane; (B) C_2–C_4 alkenes; (■) ethene, (◇) propene and (◈) sum of butenes; (C) acetylene.
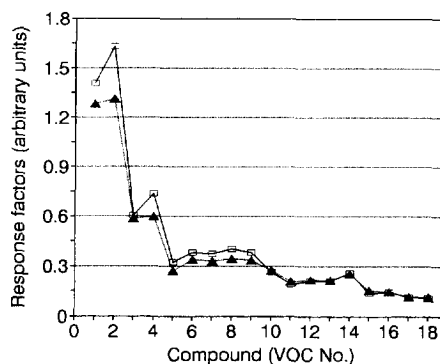

Fig. 5. Comparison of the responses given by an automated VOC monitor (▲) and our laboratory-made apparatus (□). Numbers in the abscissa indicate the same compounds as those listed in Fig. 2.
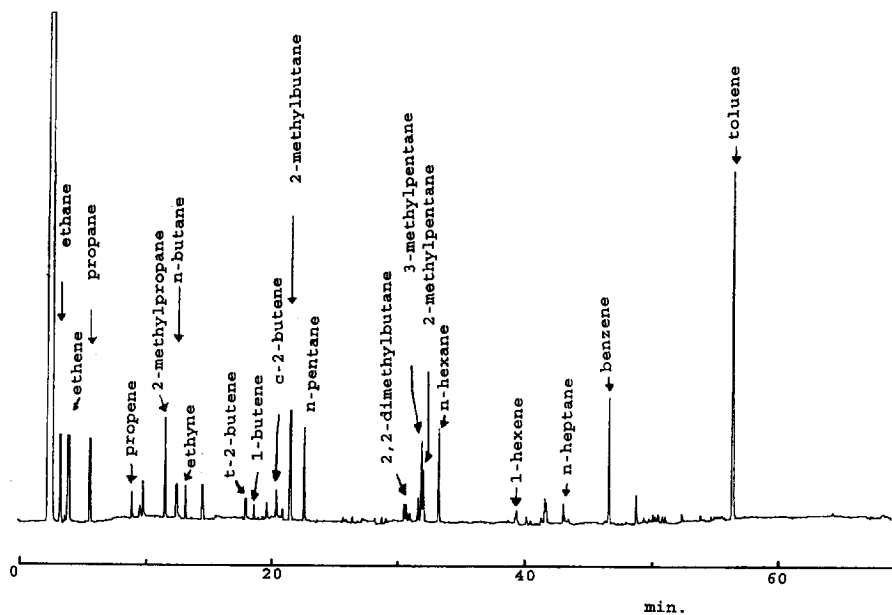
Fig. 6. Gas chromatogram of a 250-ml air sample collected at Montelibretti during the winter season.

Table 1

Mixing ratios (ppbv) of VOC-OX (C_2–C_7) recorded at the suburban site of Montelibretti, Italy, in January, 1996

Compound	Date					
	4	11	15	18	22	25
Ethane	9.31	9.53	6.79	8.77	11.30	9.14
Ethene	5.17	9.49	5.88	10.20	8.30	7.81
Propane	1.94	4.27	2.61	3.62	6.05	3.70
Propene	0.22	2.71	0.65	0.94	1.38	1.18
Isobutane	0.40	1.13	0.70	0.80	0.96	0.80
n-Butane	0.69	2.43	1.23	1.31	1.62	1.46
Acetylene	1.01	7.45	2.15	2.62	3.55	3.36
trans-2-Butene	1.07	1.22	2.01	3.27	1.52	1.82
1-Butene	0.08	0.48	0.46	0.13	0.17	0.26
2-Methylpropene	0.09	–	–	–	0.19	0.06
cis-2-Butene	0.28	0.38	0.10	0.72	0.34	0.36
2-Methylbutane	1.24	4.66	1.79	1.32	1.46	2.09
n-Pentane	0.38	–	0.66	0.48	0.44	0.39
1,3-Butadiene	–	–	–	0.14	0.15	0.06
trans-2-Pentene	–	–	–	–	0.09	0.02
cis-2-Pentene	–	–	–	–	–	–
2,2-Dimethylbutane	0.18	0.55	0.23	0.12	0.17	0.25
3-Methylpentane	0.42	1.52	0.54	0.39	0.41	0.66
2-Methylpentane	0.28	0.98	0.32	0.24	0.26	0.42
n-Hexane	0.21	6.21	0.75	0.48	0.23	1.58
Isoprene	–	0.37	–	–	0.09	0.09
1-Hexene	–	1.84	0.73	0.16	0.19	0.58
n-Heptane	0.07	0.62	0.12	0.10	–	0.18
Benzene	0.38	1.36	1.37	0.72	0.89	0.94
Toluene	0.38	2.12	0.58	0.38	0.34	0.76

All samples were taken at 12:00 h.

system was compared with that provided by an automated instrument (VOC Air Analyser, Chrompack) that is usually used in monitoring stations. The results obtained by a parallel analysis of the same air sample are shown in Fig. 5. The superior performance of our instrumentation was demonstrated by the fact that concentrations that were 15% higher than those measured by the commercial instrument were obtained for very volatile components, whereas similar values were measured for heavier components.

The linearity of our apparatus was tested using an atmospheric sample supplied by APL. Increasing volumes of that air sample (50 ml up to 350 ml) were injected into the system and good linearity was obtained. Experimental values measured for ethane, ethene, n-butane and benzene deviated from the theoretical response by no more than 10%. Through this experiment, we were also able to establish that acetylene was characterized by a normalized re-

sponse factor that was 30% lower than that of the corresponding alkane. These experiments were also useful for establishing the maximum volume of air that can be passed through the micro-trap without using devices for water removal. We found that a maximum volume of 350 ml of air with a relative humidity equal to or lower than 70% can be sampled with our apparatus. With relative humidities exceeding this value, maximum volumes were limited to 250 ml.

To increase the sensitivity down to 0.02 ppbv, a Nafion tube (1.5 m) was inserted between the sample and the cold trap. By using a 1:10 ratio between sample and desiccant flow-rates, it was possible to enrich volumes of air ranging between 1 and 2 l, with limited losses in the VOC-OX collection efficiency. The only problem found with Nafion membranes was that memory effects were sometimes observed when very concentrated samples, collected in heavily polluted urban areas, were submitted to

Table 2

Mixing ratios (ppbv) of VOC-OX (C_2–C_7) recorded in the suburban site of Montelibretti, Italy, in July, 1996

Compound	Date						
	1	4	8	11	18	22	25
Ethane	1.38	1.65	1.12	1.73	1.50	2.17	1.26
Ethene	2.53	4.45	2.39	2.05	5.38	5.14	4.37
Propane	0.84	0.60	0.22	0.82	3.52	1.01	0.77
Propene	0.39	0.60	0.46	0.36	1.12	0.48	0.74
Isobutane	0.31	0.35	–	0.23	1.34	0.48	0.35
n-Butane	0.63	0.74	0.19	0.46	2.86	1.16	0.93
Acetylene	0.33	0.37	0.11	0.21	0.26	0.35	0.39
trans-2-Butene	4.22	6.24	3.21	1.74	–	3.04	2.89
1-Butene	–	0.21	–	–	–	0.17	–
2-Methylpropene	0.12	0.30	–	0.12	0.14	0.22	–
cis-2-Butene	1.24	1.58	0.82	0.38	1.44	0.78	0.67
2-Methylbutane	0.77	1.07	0.28	0.70	1.08	1.74	1.28
n-Pentane	0.30	0.97	0.13	0.37	2.03	1.30	0.56
1,3-Butadiene	–	0.29	–	–	–	–	–
trans-2-Pentene	–	0.08	–	–	–	0.12	–
cis-2-Pentene	–	–	–	–	–		
2,2-Dimethylbutane	–	0.10	–	0.15	–	0.25	0.17
3-Methylpentane	0.16	0.20	–	0.16	0.72	0.47	0.28
2-Methylpentane	0.10	0.13	–	0.10	0.30	0.30	0.19
n-Hexane	0.63	1.14	0.11	0.22	1.14	–	0.57
Isoprene	0.43	1.35	0.36	0.42	1.12	1.26	0.85
1-Hexene	0.33	0.35	0.28	0.10	0.32	0.14	–
n-Heptane	–	0.12	–	–	0.59	0.32	0.13
Benzene	0.23	0.48	0.19	0.48	0.57	0.72	0.37
Toluene	0.62	1.12	0.34	0.51	0.63	3.87	1.05

All samples were taken at 12:00 h.

analysis. In these cases, however, the use of Nafion membranes can be avoided by reducing the volume of air to be sampled to 50–100 ml.

To date, this system has been operated in our laboratory for two years. A typical chromatogram obtained in our station during the winter season is displayed in Fig. 6. Concentrations of VOC-OX measured in winter and summer are reported in Tables 1 and 2. They were found to be quite consistent with those provided by automated apparatuses that, unlike our system, need individual calibration for very volatile VOC-OX.

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